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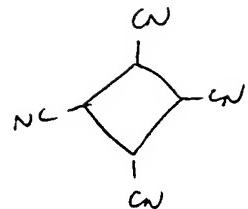
(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number: 0 532 327 A2

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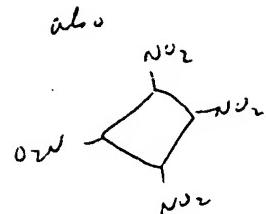
EUROPEAN PATENT APPLICATION



(21) Application number: 92308247.3

(51) Int. Cl.⁵: B01J 31/18, C07D 487/22

(22) Date of filing: 10.09.92



(30) Priority: 12.09.91 US 758148
02.06.92 US 892107

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(43) Date of publication of application:
17.03.93 Bulletin 93/11

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(54) Cyano- and polycyanometaloporphyrins as catalysts for alkane oxidation.

(57) In one embodiment, alkanes are oxidized by contact with oxygen-containing gas in the presence as catalyst of a metalloporphyrin containing cyano groups on the porphyrin ring. The catalysts may contain, in addition to cyano groups, halogen atoms on the porphyrin ring. In another embodiment, new compositions of matter comprising cyano-substituted metal complexes of porphyrins are catalysts for the oxidation of alkanes. The metal is iron, chromium, manganese, ruthenium, copper or cobalt. The porphyrin ring has cyano groups attached thereto in meso and/or β-pyrrolic positions.

EP 0 532 327 A2

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BACKGROUND OF THE INVENTION

This invention relates to oxidation of alkanes using metalloporphyrins as catalysts, and more particularly to such processes in which cyano groups have been substituted for hydrogen in the porphyrin ligand.

The use of metalloporphyrins as catalysts for the oxidation of hydrocarbons with air in the liquid phase has been shown by the inventors in U.S. Patents 4,895,680 and 4,895,682 with the further finding that halogenation of the porphyrin ring led to even more active and stable catalysts (U.S. Patents 4,900,871; 4,970,348 and U.S. Patent application Serial No. 568,118=EP-A-0 471 561). Since these discoveries, we have been able to correlate increased electron withdrawal from halogenation of the porphyrin ring to increased catalytic air oxidation activity. Je. E. Lyons and P. E. Ellis, Jr., Catalysis Letters, 8, 45 (1991).

Other functional groups besides halogens can lead to increased electron withdrawal from the metal center in metalloporphyrins. for example, cyano groups are known for their large electron withdrawing inductive effects and cyano containing metalloporphyrins with cyano groups in the beta or pyrrolic positions have been shown to be more easily reduced than their precursors without cyano substitution. R. J. Donohoe, M. Atamian and D. F. Bocian, J. Amer. Chem. Soc., 109, 5593 (1987).

DESCRIPTION OF THE INVENTION

We have now found that cyanometalloporphyrins and cyano/halogenometalloporphyrins have utility as catalysts for the air oxidation of alkanes such as methane, ethane, propane, butanes, and the like.

The catalysts of the invention are particularly effective in the oxidation of alkanes, and alkenes, including cycloalkanes, substituted alkanes and alkenes and the like. The starting materials thus include straight and branched-chain compounds having from about 1 to 2 carbon atoms, preferably 1 to 10 carbon atoms, such as methane, ethane, propane, n-butane, isobutane, n-pentane, n-hexane, 2-methylpentane, 3-methylpentane, heptane, 2-methylheptane, 3-methylheptane, the corresponding alkene forms, and the like, as well as cycloalkanes and cycloalkenes having from about 5 to 20 carbon atoms, preferably 5 to 10 carbon atoms, such as cyclopentane, cyclohexane, cycloheptane, cyclooctane, the corresponding alkene forms, and the like. These compounds, if desired, may be substituted with various moieties, although care should be taken to exclude substituents which will adversely affect the activity of the catalyst.

The oxidation, which may be carried out in a generally known manner, is desirably conducted in the liquid phase, although this is not critical, using such organic solvents as benzene, acetic acid, acetonitrile, methyl acetate, or like solvents which are inert to the conditions of the reactions, or in a neat solution of the hydrocarbon if it is liquid, and under pressures ranging from about 15 to 1500 psig, preferably 30 to 750 psig, at temperature of from about 25 to 250° C., more preferably 70 to 180° C. Depending upon whether the hydrocarbon to be oxidized is a solid, liquid or gas, it is dissolved in or bubbled through the solvent, together with air or oxygen, in the presence of the catalyst used according to the invention, for periods of time sufficient to yield the desired oxidation product, generally from about 0.5 to 100 hours, and more preferably from 1 to 10 hours.

The choice of solvent, while not critical, can have an effect on the rates and selectivities obtained and should be carefully selected in order to optimize the desired results. For example, it has been found that solvents such as acetonitrile and acetic acid are often very effective for the oxidation of alkanes to form oxygen-containing compounds, whereas reactions carried out in solvents such as methyl acetate or benzene may occur more slowly. Thus, by routine experimentation, the optimum solvent for the particular process can be readily determined.

The ratios of the various reactants may vary widely, and are not critical. For example, the amount of catalyst employed can range from about 10⁻⁴ to 10⁻³ moles per mole of hydrocarbon such as alkane, and more preferably from about 10⁻⁶ to 10⁻⁴ mole of catalyst per mole of hydrocarbon, although other amounts are not precluded; while the amount of oxygen relative to the hydrocarbon starting material may also vary widely, generally 10⁻² to 10² moles of oxygen per mole of hydrocarbon. Care should be taken since some of the ratios fall within explosive limits. As a group, the catalysts are almost always soluble unless used in large excess. Thus, as a rule, the reactions are generally carried out homogeneously.

The process of the invention comprises contacting alkane with oxygen-containing gas in the presence of a metalloporphyrin in which 12.5 to 100 percent of the hydrogen atoms in the porphyrin ring have been replaced with cyano groups. Preferably, the metalloporphyrin contains as metal, iron, chromium, manganese, ruthenium, cobalt or copper.

In one embodiment, 4 to 28 percent of the hydrogen atoms in the porphyrin ring have been replaced with cyano groups and 0 to 72 percent of the hydrogen atoms in the porphyrin ring have been replaced with halogen. For example, in a porphyrin substituted with 20 fluorine atoms and 8 cyano groups, about 28 percent of the hydrogen atoms have been replaced with cyano groups and about 72 percent of the hydrogen atoms have been

replaced with halogen atoms.

In one embodiment, 4 to 8 hydrogen atoms in the porphyrin ring have been substituted with cyano groups and 8 to 20 hydrogen atoms in the porphyrin ring have been substituted with halogen atoms.

5 In one embodiment, 1 to 8 of the pyrrolic hydrogens in the porphyrin ring have been replaced with cyano groups. In a further embodiment remaining halogens in the porphyrin ring have been replaced with halogen.

Preferably, all of the hydrogen atoms have been replaced either with cyano groups or halogen atoms, but this is not essential.

Specific catalysts useful according to the invention include cyanated meso-perfluorinatedalkylporphyrin, cyanated iron tetrakis(pentafluorophenyl)porphyrin and metallocesotetracyanoporphyrine.

10 Catalysts useful in the invention may be prepared by the following methods.

EXAMPLE 1

15 Zinc (tetrakis(pentafluorophenyl) β-octabromoporphyrine) prepared by the bromination of Zn(tetrakis-Penta-fluorophenylporphyrine) with Br₂ in CCl₄ is treated with 9 equivalents of CuCN in quinoline at reflux for several hours. After chromatography several of the bromines are replaced with CN groups giving, according to the conditions Zn(TPPF₂₀β-CN₄₋₈). The zinc is removed by mild treatment with 1M HCl and recovered by chromatography on alumina. Metals can be inserted into this H₂(TPPF₂₀β-CN₄₋₈) by treatment with the metal salt in DMF, e.g., FeCl₂ in DMF, leading to Fe(TPPF₂₀β-CN₄₋₈)Cl.

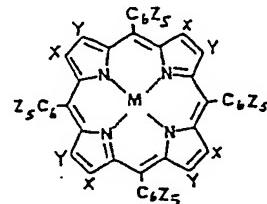
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EXAMPLE 2

If the CuCN treatment is conducted under milder conditions some of the bromine groups can be retained leading to mixed bromo/cyano metallocporphyrins. Pyrrolic positions without cyano or bromo substitution can also be brominated, chlorinated or fluorinated leading to complexes of the general structure:

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where

M is Fe, Cr, Mn, Ru, Co or Cu

X is CN

Y is CN, or Cl or Br or F

Z is H or Cl or F

EXAMPLE 3

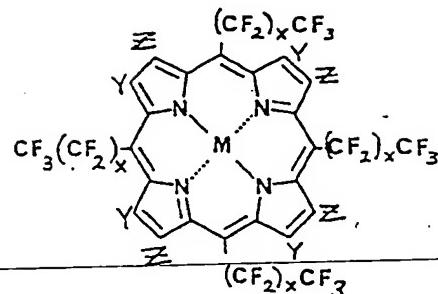
45 The conversion to cyano derivatives as disclosed in the examples above can also be applied to meso-perfluorinatedalkylporphyrins as disclosed in U.S. Patent Application Serial No. 568,118 filed August 16, 1990, (=EP-A-0 471 561) the disclosure of which is hereby incorporated by reference in this specification. The general structure of the products is:

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15 where

M is Fe, Cr, Mn, Ru, Cu, Co

X is 0-6

Y is CN

Z is CN or Cl or Br or F

20 The invention will be further disclosed with reference to the following example.

EXAMPLE 4

The catalyst prepared as described in Example 1 is used as a catalyst for the oxidation of isobutane to t-butyl alcohol in the following manner. Isobutane (6-7 grams) is dissolved in 25 ml benzene containing the catalyst, and air is added to the desired pressure. Oxidation is carried out at the designated temperature for six hours. Gaseous and liquid products are analyzed by gas chromatography and mass spectrometry. Catalyst activity is expressed as "catalyst turnovers", i.e., moles of oxygen consumed/mole of catalyst. Selectivity is the moles of TBA per 100 moles of liquid product. Higher numbers of catalyst turnovers and/or greater selectivity are obtained with the catalyst of the invention as compared with otherwise similar catalyst which has not been substituted with cyano groups. Similar results are obtained when the catalysts of Examples 2 and 3 above are used as alkane oxidation catalysts.

NEW COMPOSITIONS OF MATTER

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In this embodiment, the invention relates to metallocporphyrins useful as catalysts for the oxidation of alkanes, and more particularly to metallocporphyrins containing cyano groups on the porphyrin ring.

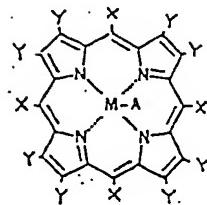
Cyano-substituted metallocporphyrins are known in the art. H. J. Callot, "Bromation de la m-tetraphenylporphine. Preparation d'alkyl - et de polycyanoporphyrines (1)", Bull. soc. chim. de France 1974, No. 7-8, pages 1492-1496, discloses copper complexes of meso-tetraphenylporphyrins having cyano substituents on one, two, three and four of the pyrrolic rings. R. J. Donohoe, M. Atamian and D. F. Boel, "Characterization of Singly Reduced Iron (II) Porphyrins", J. Am. Chem. Soc., 1987, 109, 5593-5599, disclose Fe(II)2,7,12-tricyano-5,10,15,20-tetraphenylporphyrin and Fe(II)2,7,12,17-tetracyano-5,10,15,20-tetraphenylporphyrin.

45 DESCRIPTION OF THE INVENTION

We have discovered novel cyano-substituted metallocporphyrins which contain cyano groups in meso and/or beta positions of the porphyrin ring.

The atoms or groups on the meso positions of a metallocporphyrin are represented by the X's in the following structural formula, and the atoms or groups on the beta-pyrrolic, or beta, positions by the Y's:

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where M is metal, A (1) is an anion such as chloride, bromide, fluoride, cyanide, azide, nitride, thiocyanate, cyanate, hydroxy, methoxy, chlorate, carboxylates such as acetate, propionate and benzoate, or (2) is absent, which compounds include iron complexes of μ oxo dimers wherein two structures as shown in said formula are joined through an M-O-M linkage.

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METAL COMPLEXES OF MESOCYANOPORPHYRINS

In one embodiment of the invention, the metalloporphyrin has one or more cyano groups in meso positions and has, in beta positions, either hydrogen atoms, H, or halogen atoms such as fluorine, chlorine or bromine, or nitro or cyano groups, or a hydrocarbon group or a halocarbon group. Examples of halocarbon groups are haloalkyl groups such as perfluoromethyl, perfluoroethyl and the like and haloaryl groups such as perfluorophenyl and the like. Examples of hydrocarbon groups are aryl groups such as phenyl, substituted phenyl and the like, and alkyl or cycloalkyl groups such as methyl, ethyl, cyclohexyl and the like.

In this embodiment, 1 to 4 of the X's in the above formula are CN, 0 to 3 of said X's are hydrogen, halogen, hydrocarbon or halocarbon, and Y is hydrogen, nitro, cyano, halogen, hydrocarbon or halocarbon. The Y's may all be one atom or group, or different atoms or groups

This embodiment differs from the meso-tetraphenyl cyanoporphyrins of the prior art in having cyano groups in meso positions of the metalloporphyrin complex.

30 METAL COMPLEXES OF BETACYANOPORPHYRINS

In another embodiment of the invention, the metalloporphyrin has one or more cyano groups in beta positions, and hydrogen or a substituent other than cyano in the remaining beta positions. The substituent may be halo, hydrocarbon or halocarbon. In this embodiment, X in the above formula is hydrogen, halogen, nitro, cyano, alkyl, cycloalkyl or halocarbon, at least one of said Y's is cyano and the remaining Y's are hydrogen, halogen, nitro, hydrocarbon or halocarbon.

This embodiment differs from the meso-tetraphenylbetacyanoporphyrins of the prior art in having different substituents in the meso positions.

In a preferred embodiment, the compound has either halogen atoms or cyano groups in all of the beta positions. In this embodiment, X in the above formula is hydrogen, halogen, nitro, cyano, hydrocarbon or halocarbon, at least one of the Y's is cyano, and the remaining Y's are halogen.

This embodiment differs from the metal complexes of mesotetraphenylbetatetracyanoporphyrin of the prior art in having halogen substituents in beta positions.

Substituents in the meso positions of the metalloporphyrins of this embodiment may be aryl groups such as phenyl, or they may advantageously be perhalocarbon groups such as perfluoromethyl, perfluoroethyl and the like. In this embodiment, X in the above formula is a perhalocarbon group, and Y is hydrogen or CN, at least one of the Y's being CN.

This embodiment differs from the metal complexes of mesotetraphenylcyanoporphyrins of the prior art in having perhalocarbon groups in meso positions of the porphyrin ring.

In each embodiment of the invention, M in the above formula is preferably Fe, Cr, Mn, Ru, Cu or Co, more preferably Fe.

The compounds of the invention are useful for example as catalysts in the oxidation of organic compounds. The manner of usage of the compounds for this purpose is disclosed in applicants' copending application Serial No. 07/758148, filed September 12, 1991, issued June 2, 1992 as Patent No. 5,118,886, the disclosure of which is hereby incorporated by reference in this application.

The terms porphyrin, porphin and porphine are used interchangeably herein to refer to the structure shown in the structural formula supra.

The following examples illustrate the invention:

Example 1**Preparation of H₂P(CN)₄ and MP (CN)₄Cl P = Porphine**

5 ZnP(NO₂)₄, zinc meso-tetraniroporphine (100 mg), is dissolved in 100 ml of glacial acetic acid. At 90-100°C, 0.5 g of KCN dissolved in 50 ml of tetrahydrofuran (THF) is dripped into the solution with stirring. The reaction is heated until TLC examination shows all of the starting material has reacted. The material is cooled, filtered and evaporated to dryness. The solid residue is washed thoroughly with water to remove excess KCN then dried and recrystallized from hot dichloromethane or chloroform/hexane. The zinc is removed during this process, leaving H₂P(CN)₄, meso-tetracyano-porphine. The metal salts of this complex are prepared by refluxing a THF solution of the H₂P(CN)₄ with the metal chloride (MCl₂·xH₂O where M is Fe, Cr, Co, Mn or Ru) until the metal is inserted and purifying by either recrystallization or chromatography.

Example 2**Preparation of Zn TPPF₂₀ β-Br₇CN and ZnTPPF₂₀ β-Br₆(CN)₂ (TPP=tetraphenylporphine)**

15 100 mg of ZnTPPF₂₀ β-Br₇ is dissolved in 90 ml of dimethylformamide. To this is added 129 mg of CuCN dissolved in 4.5 g of pyridine. The solution is stirred and refluxed for 5 hours then added to a saturated KCN solution. The porphyrin content is extracted with CH₂Cl₂ and evaporated to dryness in vacuo at 90°C to remove the pyridine in addition to the CH₂Cl₂. After chromatography on silica gel two major bands are obtained other than some starting material. The first green band elutes from the column with CHCl₃. Both bands have infrared (KBr) c-N around 2220 cm⁻¹. The first green material is identified as ZnTPPF₂₀ β-Br₇CN and the second brown band as a mixture of isomers of ZnTPPF₂₀ β-Br₆(CN)₂.

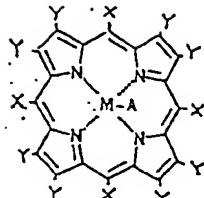
20 25 The zinc is removed by treating a CH₂Cl₂ solution of either of the cyano porphyrins with a few bubbles of HCl gas at room temperature followed by neutralization with bicarbonate solution. Complexes of metals such as Fe, Cr, Mn, Cu and Ru can be obtained by stirring the metal chloride (FeCl₂, CrCl₂, CoCl₂), or carbonyl (Ru₃(CO)₁₂) with the free porphyrin in hot dimethylformamide.

Claims

- 30 1. Process for oxidation of alkanes which comprises contacting alkane with oxygen-containing gas in the presence of metalloporphyrin in which hydrogen atoms in the porphyrin ring have been substituted with at least one cyano group.
- 35 2. Process according to claim 1 in which 1 to 8 of the pyrrolic hydrogens have been replaced with cyano groups.
- 40 3. Process according to claim 1 wherein the metalloporphyrin contains iron, chromium, manganese, ruthenium, cobalt or copper.
- 45 4. Process according to claim 2 in which remaining hydrogen atoms in the porphyrin ring have been replaced by halogens.
- 50 5. Process according to claim 4 in which 4 to 8 hydrogen atoms in the porphyrin ring have been replaced with cyano groups and in which 8 to 20 hydrogen atoms in the porphyrin ring have been replaced with halogen.
- 55 6. Process according to claim 1 in which the metalloporphyrin is a cyanated, meso-perfluorinated alkyl porphyrin.
7. Process according to claim 1 in which the metalloporphyrin is a cyanated iron tetrakis pentafluorophenylporphyrin.
8. Process according to claim 1 wherein the metalloporphyrin is a metallo mesotetracyanoporphine.
9. A new compositions of matter, useful as catalysts, compounds having the formula:

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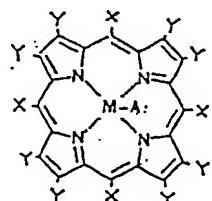


where M is iron, chromium, manganese, ruthenium, copper or cobalt, 1 to 4 of said X's are cyano, 0 to 3 of said X's are hydrogen, halogen, hydrocarbon or halocarbon, Y is hydrogen, halogen, nitro, cyano, hydrocarbon or halocarbon, and A is an anion such as chloride, bromide, fluoride, cyanide, azide, nitride, thiocyanate, cyanate, hydroxy, methoxy, chlorate, carboxylate, or is absent, said compounds including iron complexes of μ oxo dimers comprising two structures as shown in said formula joined through an M-O-M linkage.

- 10. Composition according to claim 9 wherein each X is cyano.
- 20. 11. Composition according to claim 10 wherein M is iron and each Y is hydrogen.
- 12. As a new composition of matter, a metal complex of mesotetracyanoporphyrin or mesotetracyanoporphyrin halide, where the metal is iron, chromium, manganese, ruthenium, copper or cobalt.
- 25. 13. Composition according to claim 9 wherein A is chloride, bromide, fluoride, hydroxy or azide.
- 14. Composition according to claim 9 wherein said compound is said iron complex of μ oxo dimer.
- 30. 15. As new compositions of matter useful as catalysts, compounds having the formula:

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where M is iron, chromium, manganese, ruthenium, copper or cobalt, X is hydrogen, halogen, nitro, cyano, alkyl, cycloalkyl or halocarbon, at least one of said Y's is cyano the remaining Y's are hydrogen, halogen, nitro, cyano, hydrocarbon or halocarbon, A is an anion such as chloride, bromide, fluoride, cyanide, azide, nitride, thiocyanate, cyanate, hydroxy, methoxy, chlorate, carboxylate, or is absent, said compounds including iron complexes of μ oxo dimers comprising two structures as shown in said formula joined through an M-O-M linkage.

- 45. 16. Composition according to claim 15 wherein said remaining Y's are halogen.
- 50. 17. Composition according to claim 15 wherein each X is fluorocarbon.
- 18. As a new composition of matter, useful as a catalyst, an iron complex of mesotetrafluoroalkyl/betacyanoporphyrin or mesotetrafluoroalkyl/beta cyanoporphyrin halide, having 1 to 7 carbon atoms in said alkyl group.
- 55. 19. As a new composition of matter, a metal complex of mesotetraphenyl β -heptabromo β -cyanoporphyrin, where said metal is iron, chromium, manganese, ruthenium, copper or cobalt.

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20. As a new composition of matter, a metal complex of mesotetraphenyl β -hexabromo β -dicyanoporphine, where said metal is iron, chromium, ruthenium, copper or cobalt.
21. Composition according to claim 15 wherein said compound is said iron complex of μ oxo dimer.

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